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# Technologies for CFC (Chlorofluorocarbons)/Halon Destruction

Radian Corp., Research Triangle Park, NC

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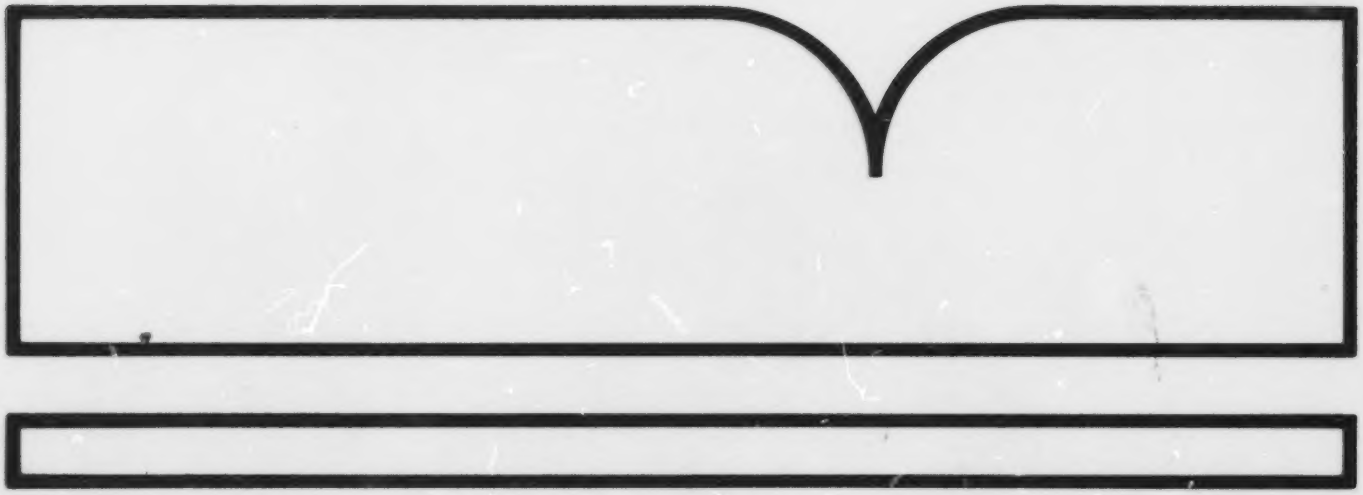

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# TECHNOLOGIES FOR CFC/HALON DESTRUCTION

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## ABSTRACT

This report presents an overview of the current status of possible technologies used to destroy chlorofluorocarbons (CFCs) and halons, chemicals implicated in the destruction of the stratospheric ozone layer. The Montreal Protocol, an international treaty to control the production and consumption of these chemicals, allows countries to increase production by the volume of CFCs or halons destroyed, if the destruction technology has been approved by the Parties to the Protocol. The Parties have neither yet approved nor considered possible destruction technologies. This document is the first step in the United States' review of such technologies, and will serve as the basis for additional work in this area.

This report is based on publicly available articles and reports, and personal contacts with various individuals who are knowledgeable in the field. The summary of the key findings addressed the following areas:

- The ability of the various technologies to effectively destroy CFCs;
- The environmental consequences of such destruction;
- The ability of current emission monitoring systems to verify that the CFCs have indeed been destroyed;
- The impacts of current regulations on CFC destruction; and
- The existence of any significant data gaps, along with recommendations of future required work to resolve any unanswered issues resulting from the data gaps.



NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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# SECTION 1

# INTRODUCTION

This report presents an overview of the current status of possible technologies used to destroy chlorofluorocarbons and halons, chemicals implicated in the destruction of the stratospheric ozone layer. The Montreal Protocol, an international treaty to control the production and consumption of these chemicals, allows countries to increase production by the volume of CFC or halon destroyed, provided that the destruction technology had been approved by the Parties to the Protocol. The Parties have not yet approved nor considered possible destruction technologies. This document is the first step in the United States' review of such technologies, and will serve as the basis for additional work in this area.

## PURPOSE OF STUDY

The U.S. Environmental Protection Agency (EPA) has requested an investigation into several areas related to destruction technologies:

- A review of the currently and potentially available destruction technologies:
- a review of potential environmental or health effects posed by destruction by-products; and
- review of methods to monitor destruction efficiency.

## METHODOLOGY/APPROACH

Due to the limited scoping exercise of this assignment, this report is based on publicly-available articles and reports, and personal contacts with various individuals who are knowledgeable in the field (see Section 3).

Results of this evaluation are presented in the following sections. Section 2 presents a summary of the key findings which include:

- The ability of the various technologies to effectively destroy CFCs;
- The environmental consequences of such destruction;
- The ability of current emission monitoring systems to verify that the CFCs have indeed been destroyed;
- The impacts of current regulations on CFC destruction; and
- The existence of any significant data gaps, along with recommendations of future required work to resolve any unanswered issues resulting from the data gaps.

Section 3 contains the bibliography for this report. This report also includes a series of Appendices. The first consists of a list of experts in this field. Other appendices provide technology overviews of the most promising destruction technologies including their relative advantages and disadvantages, a preliminary listing of technologies which were considered, trial burn data tables, a brief description of phone contacts, and information on CFC destruction provided by the Japan Ministry of International Trade and Industry (MITI).

## SECTION 2

## SUMMARY OF KEY FINDINGS

### GENERAL COMMENTS

#### CFCs and Halons are Difficult to Destroy

CFCs and halons are very stable compounds. They are resistant to oxidation, thus making them difficult to destroy by incineration. Furthermore, CFCs and halons are nonflammable and do not support combustion by themselves (halons are primarily used as fire extinguishing agents). The stability of these chemicals is attributed to the presence of fully-substituted halogens.

CFCs and halons may be broken down by hydrolysis. Hydrolysis involves splitting the CFC with water as shown in the example below for CFC-12:

$$CCl_2F_2 + 2H_2O \text{ ----> } CO_2 + 2HF + 2HCl$$

This reaction occurs in the combustion chamber of an incinerator, where supplemental fuel is burned to create the high temperature (to increase the reaction rate) and also furnish some of the water for hydrolysis.

The primary products of CFC or halon destruction are carbon compounds [such as carbon dioxide ($CO_2$)] and potentially corrosive and dangerous halogen acids [such as hydrogen chloride (HCl) and hydrogen fluoride (HF)]. It is also possible to form free halogen gases [such as chlorine ($Cl_2$), or fluorine ($F_2$)] which are also corrosive and hazardous chemical by-products.

## Potential Volume of CFCs and Halons to be Destroyed

The Montreal Protocol allows Parties to the Protocol to implement a system of credits that allow CFC and halon production and use to be offset by their destruction. In order to estimate the potential magnitude of such a program which would grant "production credits" for destroying CFCs or halons, this section examines those end use applications which would be attractive sources of CFCs for capture and destruction.

Examples of end use applications which contain CFCs or halons that could be captured and destroyed are:

- Refrigeration systems;
- Halon fire extinguishers;
- Rigid polyurethane foam;
- Solvent uses; and
- Sterilant gas systems.

The estimated inventory or "bank" for these applications in the U.S. is shown in Table 1 which indicates that over one million metric tons of CFC and halons exist. The banked emission sources store or retain the CFCs over a period of months or years. Most of the banked CFCs or halons are only emitted when the product is disposed. Depending on the application, some of the banked CFCs and halons may be recycled or destroyed rather than emitted.

Among the major categories, those sources which contain concentrated CFCs or halons (e.g., refrigeration or solvents) would be the better candidates for destruction. In contrast, the banked CFCs contained in rigid polyurethane foam will be less attractive for destruction because of the more dilute CFC content as well as the difficulties of collection and transportation.

TABLE 1. ESTIMATED U.S. BANK OF CFCs AND HALONS IN 1988
BY END USE AND COMPOUND (in Metric Tons)

| End Use | CFC-11 | CFC-12 | CFC-113 | CFC-114 | CFC-115 | H-1211 | H-1301 |
|---|---|---|---|---|---|---|---|
| Mobile Air Conditioners | | 110,000 | | | | | |
| Other Refrigeration (a) | 187,200 | 194,130 | | 1,140 | 16,740 | | |
| Rigid Polyurethane Foam (b) | 467,000 | 71,600 | | | | | |
| Other Foams | | 30 | | | | | |
| Sterilization | | 11,500 | | | | | |
| Solvents | | | 50,200 | | | | |
| Total Flooding Systems | | | | | | 270 | 24,300 |
| Portable Extinguishers | | | | | | 18,700 | 1,150 |
| Total | 654,200 | 387,260 | 50,200 | 1,140 | 16,740 | 18,970 | 25,450 |

NOTES:

a) Includes: building chillers, home refrigerators & freezers, other refrigeration appliances, refrigerated transport, cold storage warehouses, retail food storage, process refrigeration, and liquid food freezing.

b) Excludes flexible polyurethane foam (no banked CFCs).

## TECHNOLOGIES TO DESTROY CFCs AND HALONS

There are many technologies that could potentially be used to destroy CFCs and Halons (see Table 2 and Appendices B and C). Most of these technologies are at a preliminary level of development for application to CFCs and halons. Only thermal incineration is currently available and demonstrated for CFC and halon destruction. The following section presents a brief discussion of each potentially applicable technology.

### Existing and Future Technologies for Destruction

Destruction technologies can be divided into several broad classes. These include thermal, chemical, biological, and electrical (see Table 2). Contacts both with firms engaged in the disposal of hazardous wastes and producers of CFCs indicate that current practice is limited to thermal destruction processes (i.e., conventional thermal incineration).

Thermal destruction processes achieve destruction of the CFC or halon molecules by exposure to high temperatures for relatively long residence times in the presence of excess oxygen. CFCs and halons do not have enough heat of combustion to provide the temperatures necessary for thermal incineration. The necessary heat must be supplied through firing a supplemental fuel or by co-firing other wastes that have a substantial net heat of combustion.

The thermal decomposition of CFCs and halons produces either halogen acids (HCl, HF, HBr) or free halogen molecules ($Cl_2$, $F_2$, $Br_2$). These decomposition products are very corrosive and pose one of the most significant problems in CFC/halon destruction. In particular, the attack on the refractory materials used to insulate and protect the incinerator walls has been a problem, requiring development of special refractory materials. The halogen acids or free halogens must also be scrubbed from the stack gases before emission. This can be done using a water scrubber for the acid species, but the free halogen species require an alkaline scrubbing liquor. The decomposition products can be forced towards the easier to scrub halogen

TABLE 2.

SUMMARY OF EXISTING AND PROMISING FUTURE DESTRUCTION TECHNOLOGIES

| Process Classification | Process | Description | Development Status |
|---|---|---|---|
| Thermal Processes | Thermal Incineration | Destruction or dissociation of CFCs or halons by exposure to high temperature in the presence of excess oxygen. | Commercially available for CFCs and halons, both for dedicated CFC or halon destruction and for co-firing with other waste materials. |
| | Catalytic Incineration | Destruction or dissociation of CFCs or halons by exposure to lower temperatures than thermal incineration in the presence of a solid catalyst and excess oxygen. | Commercially available for other waste materials, but only at bench scale research level for CFCs and halons. |
| | Pyrolysis | Destruction or dissociation of CFCs or halons by exposure to high temperatures in the absence of oxygen. | Commercially available for other waste materials, but only at bench scale research level for CFCs and halons. |
| Chemical Processes | Metals Scrubbing/ Destruction | Active metals (such as sodium, zinc, or aluminum) suspended in an inert liquid medium chemically dehalogenate the CFCs or halons, producing a metal salt (e.g., NaCl). | Pilot scale research level. |
| | Chemical Scrubbing/ Destruction | Highly alkaline, non-aqueous scrubbing liquor absorbs and destroys CFCs and halons. | Laboratory scale research level. |
| | Wet Air Oxidation | Moderate temperature aqueous stream with oxygen destroys organic materials by oxidation, and possibly by hydrolysis for CFCs and halons. | Commercially available for other waste materials, but only bench scale research level for CFCs and halons. |

TABLE 2.

(Continued)

| Process Classification | Process | Description | Development Status |
|---|---|---|---|
| Chemical Processes (Continued) | Supercritical Water Oxidation | Similar to Wet Air Oxidation, but at supercritical conditions (higher temperature and pressure), to increase the reaction rate. | Commercially available for other waste materials, but only bench scale research level for CFCs and halons. |
| Biological Processes | No promising processes were identified | Destruction of CFCs or halons by microbial attack. | Commercially available for other waste materials, but only at conceptual research level for CFCs and halons. |
| Electrical Processes | Corona Discharge | High voltage discharge generates an ionized corona field and the energized electrons from the field are capable of dissociating many types of wastes. | Bench scale for other waste materials, but only at conceptual research level for CFCs and halons. |



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acids by providing ample hydrogen in the incinerator. The hydrogen may be supplied by a high-hydrogen supplemental fuel (like natural gas) or through steam or water injection. Figure 1 illustrates an incinerator with associated scrubber and auxiliary equipment.

Thermal incineration is the only technology for CFC or halon destruction that was found to be currently available at commercial scale. Examples of dedicated CFC incinerators were found, as well as general hazardous waste incinerators that can co-fire CFCs with other wastes. The dedicated CFC incinerators were found only at CFC manufacturing facilities (e.g., DuPont and Pennwalt in the United States, ICI in Great Britain, and Hoechst A.G. in West Germany). The co-fired CFC incinerators were found at commercial hazardous waste disposal facilities (e.g., Rollins, GSX, LWD, and Chemical Waste Management). The co-fired incinerators are limited by permit as to how much CFC they can feed, with limits ranging from a maximum of 5 percent to as little as 100 parts per million.

Other technologies have been proposed for destruction of CFCs or halons. Some of these technologies have been commercially used for destruction of other types of wastes, but they have not been demonstrated for CFCs and halons. Each of these promising technologies is discussed below.

- Catalytic Incineration is similar to thermal incineration, but the destruction is achieved at lower temperatures by use of a catalyst. The lower temperatures represent a potential savings in fuel costs, but the application to date, of catalytic incineration has been limited to destruction of hydrocarbons or chlorinated organics. If tests of chloride-resistant catalysts are successful with CFCs or halons, catalytic incineration could be commercially available in the near term (3 to 5 years).

- Pyrolysis is destruction using high temperatures, but without excess oxygen for direct combustion. This approach offers potential for reduced exhaust gas volume (resulting in smaller, less costly gas scrubbers), but has not been tested with CFCs or halons. If demonstration tests were initiated, pyrolysis could be commercially available for CFCs or halons in the near term (3 to 5 years).

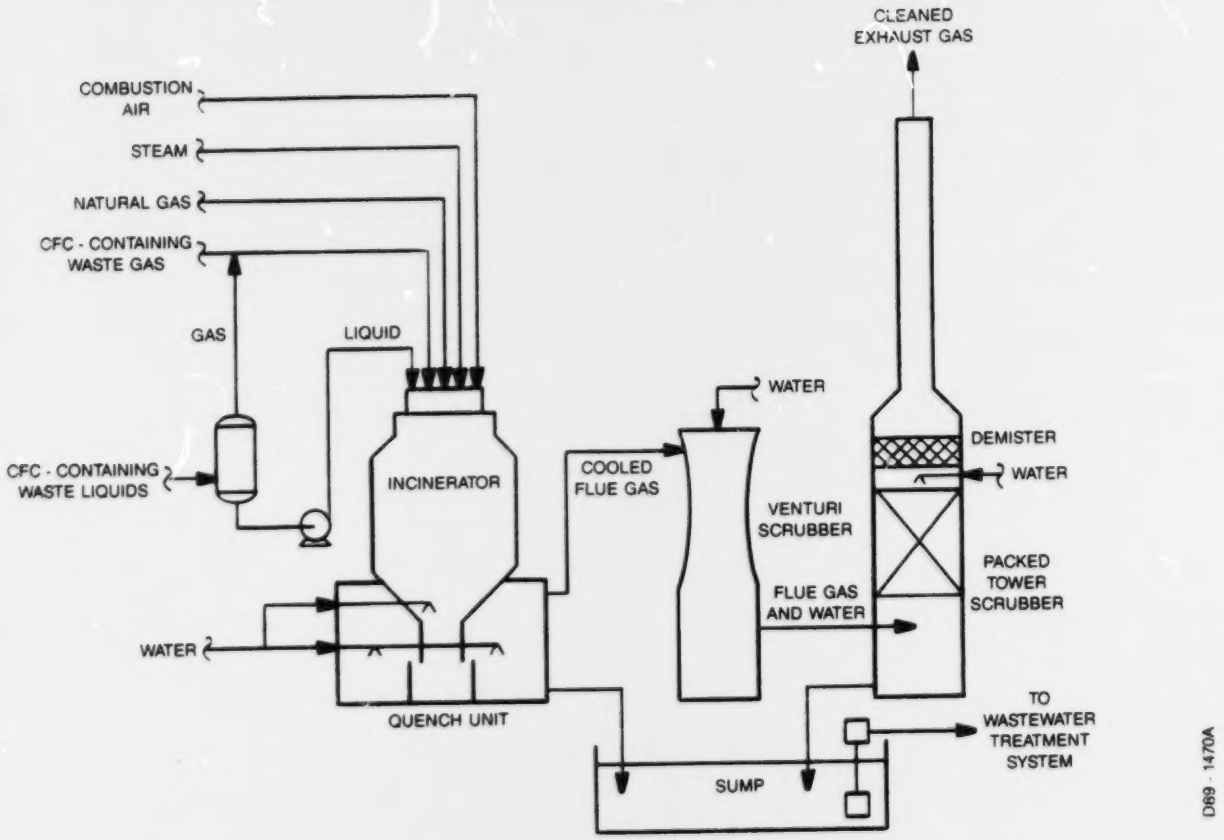


Figure 1. Simplified Flow Diagram of a Thermal Destruction Process

- Active metals scrubbing is a process which uses sodium, zinc, or aluminum metal to rapidly react with halogenated compounds. It has only been commercialized for destruction of PCB-containing wastes. Active metals scrubbing could be commercialized in the moderate term (5 to 10 years).

- Chemical scrubbing is a process that uses a highly alkaline reagent to destroy halogenated compounds. It has only been demonstrated on the bench-scale for PCB destruction. Chemical scrubbing would probably be a long term commercial possibility (10 to 15 years).

- Wet air oxidation is a process that uses a moderate temperature aqueous stream with oxygen to destroy organic compounds. Limited test data show that CFC-113 can be destroyed by this process, but its use is limited to dilute aqueous wastes. The ultimate application of wet air oxidation is questionable because of the requirement for a dilute aqueous form, but it could probably be commercialized for some CFC or halon applications in the moderate term (5 to 10 years).

- Supercritical water oxidation is similar to wet air oxidation, but it operates at higher temperatures and pressures. The current application of supercritical water oxidation is limited to destruction of aqueous wastes containing chlorinated organics. It is possible that this technology could be commercialized for specialty CFC or halon streams in the moderate term (5 to 10 years).

- Corona discharge is a process that uses energized electrons from an ionized corona field to destroy many organics. It is currently a development project, but shows possibility for future development. The commercialization of corona discharge for destroying CFCs or halons is a long term possibility (10 to 20 years).

CFC Destruction Efficiencies

A common measure of the performance of a CFC destruction technology is its destructions and removal efficiency (DRE), which is an indicator of the amount of input feed material that actually gets destroyed or removed. Although there are limited amounts of actual test burn data on CFCs, the available data show high destruction efficiencies. For example, a trial burn at Olin Corporation (Brandenburg, KY) in November 1984 showed a DRE of >99.9998 percent for co-fired CFC-11 and CFC-12 (2). To put this destruction efficiency into perspective, if 100 kilograms of CFC-12 were fed to a destruction device with a destruction efficiency of 99.9998 percent, only 20 grams of CFC-12 would be released. Appendix D presents additional trial

burn data conducted with CFCs in the waste feed. Most of this data is on CFC-11 and CFC-12. Since these are two of the most stable CFCs, it is anticipated that other CFCs (like CFC-113) would have similar, or possibly slightly better, destruction efficiencies.

Lack of Halon Destruction Efficiency Data

Information on the destruction of halons has been difficult to obtain. Inquiries to halon producers did not yield any information nor are there any publicly available test data. Sweden is beginning a research program to study destruction technologies for CFCs and halons, but tests to date have been limited to the bench scale, and no results are available. Halons do not actually "burn," and in fact their primary use is as a fire suppressing. They will thermally decompose, however, so the application of thermal destruction processes is feasible. There is believed to be some concern over generation of free bromine in a thermal decomposition process, so careful control of the combustion conditions and supplemental fuels would be required.

## ENVIRONMENTAL IMPLICATIONS OF CFC DESTRUCTION

Environmental concerns surrounding CFC and halon destruction include possible formation of potentially hazardous products of incomplete combustion (PIC), and acid and/or halogenated gas emissions. Although the acid gases can be scrubbed, the scrubber by-products create the need for disposal and handling.

### PIC Formation

Incineration processes for CFC or halon destruction require supplemental fuel, such as methane or propane, or other hydrocarbon-containing wastes to sustain combustion. Co-firing waste fuels with CFCs or halons may make it more difficult to control formation of incomplete combustion products or PICs, since waste fuels are often complex mixtures containing aromatic compounds.

Some of the aromatic compounds may become partially halogenated as the CFCs or halons are destroyed which can result in release of halogenated aromatic compounds which as a class, have been shown to be toxic.

PIC formation, in general, is a poorly understood phenomena, which is further complicated for CFC destruction systems since no data on PIC formation exist. Incomplete combustion products are formed due to localized areas of poor mixing of fuel and oxygen, and temperature deficiencies in the incinerator. Data from hazardous waste incinerators have indicated that PIC formation in a properly operated system is typically less than 1 ppm. At these low levels, the volumes of any PIC's formed would be small. The overall toxicity, however, is an unresolved issue that requires additional data to resolve.

Acid Gases

Thermal destruction of CFCs or halons also produces acid gases (HCl, HF, or hydrogen bromide [HBr]) and/or free halogen gases (chlorine ($Cl_2$), fluorine ($F_2$), or bromine [$Br_2$]) when the halogen-containing parent compound is broken down in the incinerator. Although both types of gases are hazards because of their toxicity and corrosivity, acid gases can be more easily scrubbed from the exhaust gases and are, therefore, less of a problem than the free halogen gases from a pollution control perspective. Excess hydrogen or water is desirable because it promotes the formation of acid gases rather than the free halogen gases.

Large quantities of acid gases are generated by thermal destruction of CFCs. For each pound of CFC-12 incinerated, roughly 0.6 pounds of HCl and 0.3 pounds of HF are produced. The current environmental permitting regulations for hazardous waste incinerators require that HCl emissions be controlled below 1.8 kg/hr or removed at an efficiency of 99 percent, whichever is greater (4). At present, there is no federal regulation directly applicable to HF or HBr emissions, although state or local agencies may set conditions in operating permits.

Removal of the acid gases requires scrubbing with either a water or caustic solution to react with the acid/halogen gases. Both water and caustic scrubbers are used for cleaning CFC destruction flue gases. These aqueous waste streams must be sent to wastewater treatment facilities before discharge. Large quantities of waste salts are generated. For each pound of CFC-12 incinerated, neutralization of the acid gases produced results in the generation of roughly 1.5 pounds of salts.

Combustion Products

In addition to PIC formation and the formation of acid gases, destruction of CFC's will also produce such combustion products as carbon dioxide ($CO_2$), water, nitrogen oxides ($NO_x$) and carbon monoxide (CO). These combustion products include "criteria" pollutants (e.g., $NO_x$ and CO), as well as so-called "greenhouse" gases (e.g., $CO_2$ and $NO_x$). However, the relative amount of greenhouse gases that would be emitted from the destruction of CFC's is very small when compared to the amount of similar combustion products emitted by the power generation industry and from automobiles.

MONITORING METHODS FOR CFC DESTRUCTION

To monitor destruction, record keeping procedures must be in place to track the quantities of CFC compounds in the waste fed to the incinerator, and then methods must be available to monitor the destruction efficiency achieved during incineration.

Tracking Procedures

The basic tracking procedure now in use involves the preparation of a feed record and a certificate of destruction for each waste load that is incinerated. The feed record includes information on the weight and composition of the waste load. This information is gathered when the waste load is received by the incinerator facility. After the waste has been

incinerated, the certificate of destruction is prepared to document that the waste was destroyed. This certificate is sent to the waste originator to complete the recordkeeping process.

As discussed above, information on both the weight and composition of each waste load is documented in the feed record. It was indicated during the phone contacts with incinerator operators that wastes containing CFCs or halons may arrive at an incinerator facility in drums, tank trucks, or tank cars. Scales located at the facility are used to obtain gross weights on the containerized waste loads. Information on the empty (tare) weights of the containers are then used to determine the net weight of each waste load, and this weight is then entered on the feed record.

Composition information on each waste load is obtained by chemical analysis. Typically, both the waste generator and the incineration facility operator analyze a composite sample of each waste load. The generator normally provides the results of his analysis with the waste shipment. The analysis performed by the incinerator facility then serves as a check on the information provided by the generator. The composition information obtained from this two-step process is entered on the feed record along with the net weight of the waste load.

Although it is possible to determine the quantity of waste CFCs or halons fed to the incinerator based on the weight and composition information entered on the waste feed record, extra care is required to obtain a representative sample if a waste is not homogeneous. In addition, if a waste load is stored in tanks at the incinerator facility prior to destruction, CFCs and halons may be emitted to the atmosphere. For this reason, the waste should be analyzed just prior to incineration so that a more accurate measure of the CFC or halon content is obtained.

Determination of Destruction Efficiency

As discussed above, incineration has been demonstrated as an effective technology for destruction of wastes containing CFCs. Performance standards developed by EPA under the Resource Conservation and Recovery Act (RCRA) apply to incinerators burning wastes that contain CFCs. The approach adopted by EPA is to require prelicense testing or a trial burn on each waste incinerator unit to 1) ensure that the requisite destruction and removal efficiency (DRE) is demonstrated; and 2) define a range of operating parameters for which the unit would be in compliance. During a trial burn, a 99.99% DRE for each principal organic hazardous constituent (POHC) in the waste feed must be attained. The POHCs are selected on the basis of projected high concentration in the waste stream, large annual volumes, and/or high resistance to combustion. The current RCRA incineration standards regulate only the POHCs. Emissions of products of incomplete combustion (PICs) are not covered by the standards, although future rulemaking may indirectly regulate PICs through limitations on CO.

RCRA also requires that if HCl stack emissions are greater than 1.8 kg/hr, at least 99 percent removal of HCl from the exhaust gas is required during the trial burn. RCRA incinerator operating permits will also specify continuous monitoring of CO concentration in the stack gas, with an operating limit of 100 parts per million by volume (ppmv). Additional requirements may also be specified by the State or local agency on the incinerator performance depending on waste feed composition (e.g., limitations on HF or HBr emissions). During the trial burn, incinerator operating parameters monitored include temperature, waste feed composition, waste feed rate, combustion air velocity, residence time, $O_2$, and CO.

Once the license to operate the incinerator is granted, the license mandates that operating parameters be selected from the range specified during the trial burn. The permit is generally valid for five years. During this period, the federal or the designated state agency conducts, at a minimum, annual inspections of the incinerator operation, including records on CO,

temperature, waste feed, waste composition, and scrubber operation. Any change in incineration operation (e.g., waste feed rate, composition, combustion temperature), other than what was represented in the permit application or is allowable under the permit, requires a modification be made to the permit, with a potential requirement to conduct another trial burn.

Sampling and Analytical Methods

Measurement of several incinerator operating parameters are necessary to maintain thermal destruction conditions which are equivalent to those observed during a successful trial burn. The principal candidate species for continuous monitoring is one of the compounds selected for the trial burn. However, the sampling and analytical methods are not practical for continuous performance monitoring on a day to day basis. One alternative is to indirectly monitor incineration performance using commercially available continuous monitors to measure combustion intermediates (e.g., CO or hydrocarbons) and thereby infer waste destruction efficiency. CO is a good indicator of incomplete combustion (the lower the CO level, the more complete the combustion) and is therefore often used as a surrogate indicator of combustor performance. Currently, continuous monitoring of CO concentration in the stack is the only RCRA requirement after a permit is granted.

Several studies have been conducted to determine if incinerator emissions can be correlated with surrogate compound, like CO or total hydrocarbon, concentrations in the stack gases. Some of these studies have shown a relationship between CO and/or total hydrocarbon concentrations and incinerator emissions while other studies have found no correlation. It should be noted that these studies have been done on other types of wastes, not CFCs or halons. Therefore, additional research needs to include not only the validation of the PIC to surrogate correlation approach, but also the applicability of that approach to CFCs and halons.

## IMPLICATIONS FOR DESTRUCTION

This section highlights a number of issues which will likely effect the implementation of a CFC destruction program.

### Need for Central Facilities

Destruction processes for CFCs and halons are likely to be operated as a central facility, rather than as portable or user-sited units. This is because 1) destruction facilities must comply with stringent regulations (and it is simpler and less costly to permit a few central facilities, rather than a multitude of smaller units); and 2) considerable expertise is required to safely and efficiently destroy these compounds, which is not generally available to the user population. A central destruction facility would require that individual users collect and transport the compounds for disposal. As such, it is likely that current CFC manufacturing and recycle facilities, and commercial hazardous waste incineration facilities will be the location of most destruction facilities. This is because many of these facilities already have incinerators and have the needed technical and management expertise. It may also be easier to get permits for CFC destruction at locations which already are permitted for CFC manufacturing and recycling or waste destruction.

### Conversion of CFCs

An alternative to destruction of certain CFCs is chemical conversion into fluoromonomers. Fluoromonomers are used to make chemically-resistant plastics such as Teflon® or Kel-F® (3) as is currently practiced with partially-halogenated hydrochlorofluorocarbons (HCFC), and also with CFC-113. For example, CFC-113 is converted to chlorotrifluoroethylene which is then polymerized to form KEL-F® (sold by 3M Corporation). CFC-11 and CFC-12 also have been reacted with methane or ethylene (but only in the laboratory) to form vinylidene fluoride, which could then be polymerized to make Kynar® (sold by Pennwalt).

Limitations to this approach include: the demand for these plastics versus the amount of CFCs and HCFCs, the ability to purify the CFC/HCFC's to make saleable grade plastic and the economics. However, polymerization to a plastic whether saleable or not may be environmentally and economically more attractive than other destruction options.

Recycling of CFCs

Although recycling is not a destruction process, it is an interim measure which can be actively promoted to reduce emissions of used or contaminated CFCs and lessen the production of new CFCs. Once substitute chemicals become available to replace CFCs or halons, recycling should ease the transition by providing users a continuing supply of the regulated compounds.

Recycling of contaminated CFCs is currently practiced on a commercial scale by Omega Recovery (Whittier, CA). Also, some solvent suppliers (such as DuPont) operate central solvent reclamation facilities. These facilities generally accept CFCs from solvent distributors or firms which service large commercial building chillers. Recovered CFCs may contain contaminants such as water, oil, other solvents, acids, and noncondensible gases. The reclamation process involves such steps as neutralization, filtration, drying or adsorption, and distillation to return the material to purity specifications which meet or exceed those for new, virgin CFCs.

Costs for recycling used CFCs were found to be in the same range as costs charged for destructing used CFCs. A significant difference exists, however, in that the recycling process produces a replacement for the used CFCs as part of the recycling cost, whereas make-up CFCs must be purchased when used CFCs are destroyed. For this reason, recycling will likely be less costly than destruction.

## REGULATORY IMPACTS

This section addresses current U.S. environmental regulations which pertain to emissions and disposal of CFCs and halons, and discusses potential regulatory changes that may affect CFC or halon disposal operations. Currently, the regulations that would have the most effect on CFC disposal operations are: 1) the Resource Conservation and Recovery Act (RCRA) which can affect the handling and processing of spent CFC wastes, and 2) the Clean Air Act which affects the allowable emissions of acid gases. All regulatory provisions should be able to be met and thus should not create impediments to implementing a CFC destruction program.

### Resource Conservation and Recovery Act (RCRA)

The Resource Conservation and Recovery Act (RCRA) establishes the Environmental Protection Agency's authority to regulate solid and hazardous wastes. The RCRA regulations require that hazardous wastes be tracked from generation to ultimate disposal.

In uncontaminated form, CFCs and halons are not regulated wastes, nor are they likely to be considered characteristically hazardous. However, as previously indicated, recovered CFCs and halons may contain contaminants controlled by RCRA. Thus, recovered CFCs and halons may be defined under RCRA as hazardous wastes by virtue of being mixed with other regulated wastes, such as solvents, or by being mixed with corrosive wastes. Thus, RCRA regulations may be applicable to CFC and halon destruction processes, such as incineration. Anticipated revisions to the current RCRA incineration rules may particularly impact CFC and halon destruction since PICs will likely be a primary focus of future changes. To the extent that recycling becomes a viable option and the CFC and halon wastes are defined by RCRA to be hazardous then the recycling provisions of RCRA may also apply.

In addition to possible application of the federal hazardous waste rules, some states (such as California) have designated contaminated CFCs as hazardous wastes due to the corrosive and acidic nature of some wastes. Designation of CFC and halon wastes as hazardous under federal and/or state laws will significantly affect the economics of destruction and recycling options, and will tend to create a disincentive to utilization of these methods.

Clean Air Act (CAA)

The Clean Air Act (CAA) establishes the authority of the U.S. Environmental Protection Agency to regulate emissions of air pollutants from both stationary and mobile sources. The CAA requires EPA to establish National Ambient Air Quality Standards (NAAQS) as well as source specific emission limits for pollutants of concern. The primary mechanism for controlling emissions is through a national permitting system that imposes technology based limits on point sources.

The Federal CAA does not directly address emissions of CFCs or halons. For example, the National Emission Standards for Hazardous Air Pollutants (NESHAPs) do not regulate these pollutants, nor is there an applicable New Source Performance Standard (NSPS). However, under Prevention of Significant Deterioration (PSD) regulations both HF and HBr emissions can fall under the CAA if they are emitted at more than 3 tons per year (TPY) from a source which also emits one or more of the six criteria pollutants (e.g., CO, $NO_x$, $SO_2$) at more than 250 tons per year.

State or local air pollution regulatory agencies may regulate CFC and halon emissions or emissions from destruction or recycling processes through their own permitting programs.

Clean Water Act (CWA)

The Clean Water Act, also known as the Federal Water Pollution Control Act, gives the Environmental Protection Agency the authority to regulate the discharge of pollutants into waters of the United States. This language has been interpreted to include virtually all U.S. surface waters and the territorial sea. The Acts primary mechanism for controlling discharge is through a national permit system which imposes technology based limits on point sources.

Effluent from CFC or halon incinerator scrubbers will require treatment before direct discharge to a watercourse under the National Pollutant Discharge Elimination System (NPDES) program or may require pretreatment before being discharged to a publicly owned treatment works (POTW). In either case, treatment of the effluent will generate sludges which may themselves be considered as RCRA hazardous wastes.

Toxic Substances Control Act (TSCA)

The Toxic Substances Control Act (TSCA) provides the Environmental Protection Agency with the authority to regulate the many chemical substances and mixtures which are constantly being developed and produced in this country. TSCA provides for the compilation of an inventory of chemicals manufactured, imported or processed for commercial purposes in the U.S. TSCA gives the Environmental Protection Agency broad authority to regulate chemicals found to pose unreasonable risk to human health or the environment. The statute specifically requires the phase-out of the manufacture of polychlorinated biphenyls (PCBs) except for uses that are "totally enclosed."

Fully halogenated chlorofluoroalkanes (in aerosol propellant use) are subject to certain manufacturing, processing, and distribution in commerce restrictions under TSCA (40 CFR Part 762) except as otherwise exempted. Other than these restrictions, the TSCA rules do not address CFC and halon use or disposal.

Comprehensive Environmental Response Compensation and Liability Act (CERCLA)/ Superfund Amendments and Reauthorization Act (SARA)

The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) provides federal authority for responding to releases of hazardous substances into the environment. The Act created a "Superfund" generated from taxes levied on the chemical and petroleum industries which produce the hazardous substances specified in the implementing regulations. The fund is used to respond to sites where uncontrolled hazardous substances are found; though liability for the cleanup ultimately belongs to the parties responsible for the contamination.

The Superfund Amendments and Reauthorization Act (SARA) provides for the continuation of the provisions of CERCLA and strengthens many of its parts. In addition to the $8.6 billion provided by the Amendments for site remediation, SARA seeks to streamline the clean-up process, to require that permanent solutions be used, and to increase the citizen participation and access to the site remediation activities. In addition, Section 313 of SARA establishes reporting requirements for all compounds regulated by the Act.

CFC-113 is included in the list of toxic chemicals for Section 313 of SARA. Under these rules, producers and users of CFC-113 must comply with the reporting provisions of Section 313 which require annual estimates of routine substance releases to air, water, or ground.

DATA GAPS AND RESEARCH NEEDS

Four major areas of data gaps identified in this evaluation are: 1) PIC formation resulting from CFC destruction; 2) technical design data on CFC thermal destruction systems, particularly in the area of corrosion and materials of construction; 3) all aspects of halon destruction; and 4) availability of continuous CFC or halon monitors to verify destruction.

These data gaps can be addressed through short-term (2-5 years) research initiatives which would be focused on better characterizing thermal destruction systems to make data available for future developments. In addition to short-term research initiatives, a more long-term (5-15 years) research program should also be considered to promote the development of the most promising destruction technologies now in various stages of development.

Short-Term Research Initiatives (2-5 years)

The objective of short-term research is to quickly resolve any data gaps that exist with the current technology so that existing concerns over secondary environmental impacts and specialized design requirements can be resolved. A viable program could consist of three main elements:

1. Characterization of Thermal Destruction Systems--Several issues/data gaps exist concerning CFC destruction which could readily be resolved through a well-designed fundamental research program. This fundamental research can be supported by field tests at selected commercial or pilot-scale facilities. Issues that can be resolved through short-term research are:

    a. CFC PIC Formation--Under what operating conditions are they formed? How does the role of mixed fuel firing affect PIC formation? Are there any potential human health effects from exposure to PICs? One approach to generate some PICs and health effects data would be to require PICs sampling and analysis as part of the RCRA trial burns.

    b. Specialized Design Requirements--Correlations of corrosive off-gases as a function of operating conditions will determine how to minimize free halogen species, and will provide data for specifying appropriate materials of construction for future designs, and for designing the acid gas scrubbing systems.

    c. Halon Destruction Data--Since no data currently exists, the test program could be designed to answer: What operating conditions and supplemental fuel requirements are necessary for Halon destruction? What materials of construction are required? What conditions will result in PIC formation? What is the Destruction Efficiency? What is the proportion of free bromine to HBr? What type of scrubbing is require to control bromine and/or HBr emissions?

2. Develop accurate cost estimates for a CFC/Halon destruction using the results of the data from the fundamental research and demonstration programs.

3. Develop approved monitoring techniques. CFC Monitoring--Either initiate development of continuous monitors to verify the destruction of CFCs and halons or conduct studies to correlate CFC/halon destruction other easily monitored surrogate parameters (e.g., carbon monoxide, temperature, etc.).

Long-Term Research Initiatives (5-15 years)

The objective of a long-term research program would be to promote the development of some alternative CFC/halon destruction technologies. Such a program could probably begin with a detailed conceptual evaluation of all alternatives to incineration in order to prioritize their relative merits. The conceptual study could be followed by bench-scale proof-of-concept tests for the most promising alternatives, and then a pilot-scale demonstration. Also, associated cost and environmental assessments could be conducted. The overall objective would be to develop and demonstrate a superior alternative to the point that it could be commercialized by the private sector.

It is possible that some of the potential alternative destruction technologies could be adapted to CFCs or halons on a more accelerated basis. This would apply to those technologies that are already commercially available for other waste materials. It might be possible to conduct a commercial-scale test in the near term for some of these techniques, and, if successful, to make them commercially available in the near term. This type of accelerate development would best be accomplished by private industry, but EPA could help to promote such activity by developing information that demonstrates the market potential for CFC or halon destruction systems.

## SECTION 3

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## APPENDIX A

### List of Experts

(List of Experts organized by specialization, with affiliation/organization and address.)

| GENERAL AREA | NAME | ORGANIZATION | ADDRESS | SPECIFIC EXPERTISE |
|---|---|---|---|---|
| THERMAL PROCESSES | Mr. Donald A. Oberacker | U.S. EPA<br>HWERL | Thermal Destruction Branch<br>Risk Reduction Engineering Lab<br>26 West Martin Luther King Dr.<br>Cincinnati, OH 45268 | Thermal Destruction Processes<br>Trial Burn Testing<br>SITE Program |
| | Dr. Paul M. Lemieux | U.S. EPA<br>AEERL | Combustion Research Branch<br>MD-65<br>Research Triangle Park, NC 27711 | Thermal Destruction Processes<br>Products of Incomplete Combustion |
| | Mr. Joseph A. McSorley | U.S. EPA<br>AEERL | Combustion Research Branch<br>MD-65<br>Research Triangle Park, NC 27711 | Thermal Destruction Processes<br>Products of Incomplete Combustion |
| | Dr. Barry Dellinger | Univ. of Dayton<br>Research Institute | Environmental Sciences<br>300 College Park<br>Dayton, OH 45469 | Thermal Destruction Kinetics<br>Products of Incomplete Combustion |
| | Mr. Harold Diot | Ogden Environmental Services | P.O. Box 85178<br>San Diego, CA 92138-5178 | Circulating Bed Combustion System Vendor |
| | Ms. Carrie Penman | Westinghouse Electric | Waltz Mill Site<br>P.O. Box 286<br>Madison, PA 15663 | Plasma System Vendor |
| | Mr. Gene Irrgang | T-Thermal | Brook Road<br>Conshohocken, PA 19428 | Incinerator/Burner Vendor with Installations Handling CFCs |
| | Mr. Mike Keller | John Zink Co. | P.O. Box 70220<br>Tulsa, OK 74170 | Incinerator/Burner Vendor with Installations Handling CFCs |

| GENERAL AREA | NAME | ORGANIZATION | ADDRESS | SPECIFIC EXPERTISE |
|---|---|---|---|---|
| THERMAL PROCESSES (cont.) | Mr. Jack Buice | Dow Chemical USA | Texas Operations<br>OC-1120<br>Freeport, TX 77541 | Thermal Oxidation of Chlorinated Organics |
| | Mr. Jim Aker | E.I. DuPont de Nemours | "U"<br>Chambers Works<br>Deepwater, NJ 08023 | Thermal Destruction of CFCs |
| | Mr. Don Natter | Rollins Environmental | P.O. Box 609<br>Deer Park, TX 77536 | Thermal Destruction of CFCs |
| | Dr. James Spivey | Research Triangle Institute | P.O. Box 12194<br>Research Triangle Park, NC 27709 | Catalytic Destruction of Chlorinated Organics |
| | Dr. Vic Cundy | Louisiana State University | Department of Mech. Engrg.<br>Baton Rouge, LA 70803 | Thermal Destruction Kinetics<br>Products of Incomplete Combustion |
| | Mr. Joe Santoleri | Four Nines Corp. | Conshohocken, PA 19428 | Trial Burn Testing<br>Incineration Consultant |
| CHEMICAL PROCESSES | Mr. Garry Howell | U.S. EPA<br>HWERL | Risk Reduction Engineering Lab<br>26 West Martin Luther King Dr.<br>Cincinnati, OH 45268 | Chemical Destruction Processes<br>SITE Program |
| | Mr. Charles Russell | Detox International | 525 Dunham Road<br>St. Charles, IL 60174 | Active Metals Destruction (Molten Aluminum) |
| | Mr. Leo Weitzmann | Acurex | P.O. Box 13109<br>Research Triangle Park, NC 27709 | Active Metals Destruction (Acurex PCB process) |

| GENERAL AREA | NAME | ORGANIZATION | ADDRESS | SPECIFIC EXPERTISE |
|---|---|---|---|---|
| CHEMICAL PROCESSES (cont.) | Mr. Ralph Morgan | Modar | 3200 Wilcrest<br>Houston, TX 77042 | Supercritical Fluid Oxidation |
| | Mr. William Copa | Zimpro | 301 W. Military Road<br>Rothschild, WI 54474 | Wet Air Oxidation of CFCs |
| ELECTRICAL PROCESSES | Dr. Norm Plaks | U.S. EPA<br>AEERL | MD-61<br>Research Triangle Park, NC 27711 | Electrostatic Destruction (Corona Discharge) |
| OTHER AREA | Mr. Tom Hedlund | Swedish National Environmental Protection Board | Box 1302<br>S-1007125<br>Solna, SWEDEN | Sweden's Programs to Evaluate CFC/halon Destruction Technology |
| | Dr. Koichi Mizuno | Atmospheric Environmental Protection Department | Nat'l Research Instit. for Pollution and Resources<br>Ministry of International Trade and Industry (M.I.T.I.)<br>16-3 Onogawa Tsukuba<br>Ibaraki 305 JAPAN | Japan's Program to Evaluate CFC/halon Destruction Technology |
| | Dr. Hugh Reilly | Sandia National Lab | Solar Energy Department<br>Division 6227<br>Albuquerque, NM 87185 | Solar Destruction |
| | Mr. Dennis O'Meara | Omega Recovery | 12504 East Whittier Blvd.<br>Whittier, CA 90602 | Recycling Processes |
| | Dr. Louis Thibodeaux | Louisiana State University | Department of Chem. Engrg.<br>Baton Rouge, LA 70803 | Biological Processes<br>Land Treatment |
| | Mr. Dale L. Harmon | U.S. EPA<br>AEERL | MD-62B<br>Research Triangle Park, NC 27711 | CFC Control Technologies<br>Recycling Processes |

# APPENDIX B

## Control Technology Summaries

(Control Technology Summaries providing additional information on destruction processes for CFCs and halons as (1) currently practiced or (2) considered by experts to have the greatest potential for future applicability.)

## CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **CONVENTIONAL THERMAL OXIDATION**

OPERATING PRINCIPLE: Conventional thermal oxidation refers to various types of incineration processes using a high temperature flame. With CFCs or halons, the destruction process might be dissociation at the elevated temperature followed by rapid hydrolysis rather than oxidation.

DEVELOPMENT STATUS: Commercial

DESTRUCTION EFFICIENCY: Very high (>99%).

RELIABILITY/OPERABILITY: Careful selection of refractory material necessary to prevent rapid erosion by HF at high temperature. Also, combustion conditions must be maintained with excess $H_2$ or $H_2O$ to ensure formation of acid gases rather than free $Cl_2$, $F_2$, or $Br_2$ (which are generally more difficult to clean up). Incinerator should use a high energy auxiliary fuel burner to create a high temperture zone for thermal dissociation, followed by steam or water injection to effect a rapid hydrolysis of the chlorine and fluorine to form HCl and HF.

SECONDARY ENVIRONMENTAL CONCERNS: Acid gases generated by destruction of CFCs and halons include HF, HCl, and HBr. Also, there is potential for formation of toxic and hazardous products of incomplete combustion (PICs) which may also be potential ozone depleters.

COSTS - CAPITAL: Incinerator refractory may have to be expensive high alumina type.

- OPERATING AND MAINTENANCE: Fuel requirement for burner, steam or water for hydrolysis, and reagents for neutralization of acid gases. Rough calculation for fuel cost and caustic indicates approximately $0.35 per kilogram ($0.16 per pound) of CFC destroyed. Disposal costs for scrubber sludge.

LIMITATIONS/BARRIERS: Typical CFC incinerator installations are specially designed units with extensive air pollution control devices. They are often limited to firing low concentrations of CFCs to avoid severe refractory damage.

SUMMARY - PROS: Conventional thermal oxidation is currently the only available method for complete destruction of CFCs and halons. Industrial contacts contend that high destruction efficiencies and insignificant PIC formation are typical.

- CONS: Possible formation of PICs which may be toxic, hazardous, or ozone depleters. Sparse data on destruction efficiency. Refractory damage caused by HF can result in costly repairs and downtime.

CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **CATALYTIC THERMAL DESTRUCTION**

OPERATING PRINCIPLE: Catalytic thermal destruction involves using a solid catalyst to provide an alternate reaction pathway for destruction at lower temperatures than conventional thermal destruction.

DEVELOPMENT STATUS: Commercial (For CFCs: Bench-scale)

DESTRUCTION EFFICIENCY: High (>90%).

RELIABILITY/OPERABILITY: Careful selection of catalyst and construction material (esp. catalyst bed support) necessary to prevent deactivation or rapid corrosion, respectively. Conditions must be maintained with available $H_2$ or $H_2O$ to ensure formation of acid gases rather than free $Cl_2$, $F_2$, or $Br_2$ (which are generally more difficult to clean up).

SECONDARY ENVIRONMENTAL CONCERNS: There is potential for formation of toxic and hazardous products of incomplete combustion (PICs) which may also be potential ozone depleters. Also, acid gases or neutralized salts may be regulated. Disposal of used catalyst may also be a potential concern.

COSTS - CAPITAL: Potential cost savings compared to thermal incineration since reduced temperature minimizes the need for special refractory or materials of construction.

- OPERATING AND MAINTENANCE: Fuel requirement for incinerator and reagents for neutralization of acid gases. Disposal costs for scrubber sludge. Periodic replacement of catalyst.

LIMITATIONS/BARRIERS: Catalytic incineration of CFCs is an adaptation of existing technology available for destruction of chlorinated organics. However, current practice has been limited to destruction of dilute gaseous streams containing chlorinated organics. There are no data available for catalysts used for CFC destruction.

SUMMARY - PROS: The primary advantage of catalytic incineration over conventional thermal incineration is the potential cost savings from reduced fuel requirements since destruction may be possible at a lower temperature. Cost of metal oxide catalysts are lower than noble metal catalysts; metal oxide catalysts are the preferred type for this stream.

- CONS: Some early data on catalytic incineration of chlorinated organics showed rapid deactivation and low destruction efficiency with noble metal catalysts. No data on destruction efficiency for CFCs or halons. No proven technology in this area.

CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **PYROLYSIS**

OPERATING PRINCIPLE: Pyrolysis involves destruction of CFCs or halons by heating to very high temperatures in the absence of air. Since CFCs and halons can be destroyed through bond homolysis, simple heating without air is sufficent to break the bonds. This technology includes the plasma torch and other sub-stoichiometric burners.

DEVELOPMENT STATUS: Commercial (For CFCs: Bench-scale)

DESTRUCTION EFFICIENCY: Very high (>99%).

RELIABILITY/OPERABILITY: Careful selection of pyrolyzer material necessary to prevent rapid erosion by HF at high temperature. Conditions must be maintained with available $H_2$ or $H_2O$ to ensure formation of acid gases rather than free $Cl_2$, $F_2$, or $Br_2$ (which are generally more difficult to clean up).

SECONDARY ENVIRONMENTAL CONCERNS: Pyrolysis of CFCs or halons without $H_2$ or $H_2O$ would likely result in formation of free $Cl_2$, $F_2$, or $Br_2$. Also, there is higher potential for formation of toxic and hazardous products of incomplete combustion (PICs) when operating under "reducing" conditions which may also be potential ozone depleters.

COSTS - CAPITAL: Potential cost savings compared to thermal incineration since reduced gas flow may allow significantly smaller scrubbers. Some test data with pyrolysis destruction has shown a need for an incinerating afterburner to clean up PICs. This would add significantly to the cost.

- OPERATING AND MAINTENANCE: Energy requirement for pyrolyzer and reagents for neutralization of acid gases. Disposal costs for scrubber sludge.

LIMITATIONS/BARRIERS: Pyrolysis is less developed than conventional thermal oxidation for the destruction of hazardous wastes. Some critics feel that when an afterburner is required for the pyrolyzer exit gas, an incinerator alone is a more cost effective choice.

SUMMARY - PROS: The primary advantage of pyrolysis over conventional thermal incineration is the potential cost savings from smaller downstream scrubbing equipment (made possible by heating without air).

- CONS: Commercial development of pyrolysis systems may be limited by possible formation of large quantities of PICs which may be toxic, hazardous, or ozone depleters. Sparse data on destruction efficiency. Potential damage caused by HF can result in costly repairs and downtime.

CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **METALS SCRUBBING/DESTRUCTION**

OPERATING PRINCIPLE: Active metals such as sodium, zinc, or aluminium are suspended in an inert liquid medium. The active metals chemically dehalogenate the halogenated organic waste feed, producing a metal salt (e.g., NaCl).

DEVELOPMENT STATUS: Pilot-scale

DESTRUCTION EFFICIENCY: Very high (>99%)

RELIABILITY/OPERABILITY: The active metals are highly reactive with water or air. Also, there may be difficulties in terms of materials of construction.

SECONDARY ENVIRONMENTAL CONCERNS: One advantage of active metals scrubbing is that the metal salts can be precipitated out of concentrated solution in solid form, possibly allowing easier disposal of this secondary waste. Fluoride salts are a potential concern.

COSTS - CAPITAL: Moderate to low compared to baseline thermal incineration.

- OPERATING AND MAINTENANCE: For CFCs: Costs are unknown, probably high.

LIMITATIONS/BARRIERS: The primary limitation of active metals scrubbing is uncertainty regarding the ability to maintain the reactivity of the metal in the presence of air and water. Feed pretreatment might be required to remove water, and the process might have to be run under slight nitrogen pressure to exclude air.

SUMMARY - PROS: The process has been used to destroy another class of toxic chemicals which are fairly unreactive, PCBs (using the Acurex process), so there is some experience with the technique. Metals scrubbing is claimed to provide a high degree of destruction at near-ambient temperatures and may be tailored to produce a solid salt which would be easier to dispose of.

- CONS: Reaction of CFCs or halons with active metals is untested and unproven. The active metals themselves are often pyrophoric (they spontaneously react with air) or they may be water-reactive. This would complicate the operation of such a process.

CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **CHEMICAL SCRUBBING/DESTRUCTION**

OPERATING PRINCIPLE: This technology involves the use of a highly alkaline, non-aqueous scrubbing liquor to absorb and destroy halogenated organics. One example of this is the K-PEG process (KOH is the alkaline component; poly-ethylene glycol is the solvent).

DEVELOPMENT STATUS: Bench-scale

DESTRUCTION EFFICIENCY: High, but may be lower than active metals scrubbing.

RELIABILITY/OPERABILITY: The alkaline component is highly reactive with water. Absorption of carbon dioxide ($CO_2$) from air by the sorbent may be a problem. Also, there may be difficulties in terms of materials of construction.

SECONDARY ENVIRONMENTAL CONCERNS: One advantage of the K-PEG process is that the salts formed by dehalogenation can be precipitated out of concentrated solution in solid form, possibly allowing easier disposal of this secondary waste. Fluoride salts are a potential concern.

COSTS - CAPITAL: Low to moderate

- OPERATING AND MAINTENANCE: For CFCs: Costs are unknown, but may be less expensive than active metals process.

LIMITATIONS/BARRIERS: The primary limitation of chemical scrubbing with an alkaline reactant is uncertainty regarding the degree of destruction. Also, there may be limitations to treatment of water-contaminated CFCs or halons.

SUMMARY - PROS: Chemically reactive scrubbing of air streams containing CFCs or halons might be superior to ordinary scrubbing processes (such as lean oil scrubbing). The process has been demonstrated on the bench-scale for the destruction of PCBs. Control of the pH may allow precipitation of a solid salt which could be easily separated and disposed of.

- CONS: Reaction of CFCs or halons with alkaline scrubbing liquors is untested and unproven. The alkaline components are water-reactive and could be very corrosive.

CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **SUPERCRITICAL WATER OXIDATION**

OPERATING PRINCIPLE: This process involves using water at supercritical conditions (i.e., temperature > 374°C (705.5°F) and pressure > 218 atm (3208 psia)) with oxygen to achieve rapid destruction of organic compounds. With CFCs or halons, the destruction process might involve hydrolysis as well as oxidation.

DEVELOPMENT STATUS: Commercial (For CFCs: Bench-scale)

DESTRUCTION EFFICIENCY: Potentially higher than wet air oxidation.

RELIABILITY/OPERABILITY: Possible metallurgy considerations which might affect reliability/operability or produce high capital costs.

SECONDARY ENVIRONMENTAL CONCERNS: Unknown; possible neutralization of acidic aqueous waste stream. Fluoride salts are a potential concern.

COSTS - CAPITAL: Possible requirement for exotic materials of construction.

- OPERATING AND MAINTENANCE: Higher energy requirements than wet air oxidation due to higher temperature and pressure. Requires oxygen supply.

LIMITATIONS/BARRIERS: Supercritical water oxidation is a new technology which is basically a modification of wet air oxidation. Both supercritical water oxidation and wet air oxidation are typically used with aqueous streams only. Since CFCs and halons do not have an abstractable hydrogen or a double bond, they are resistant to oxidation. This may make them difficult to destroy using this process, although initial hydrolysis could occur to destabilize the target molecule.

SUMMARY - PROS: Limited data exist for destruction of CFC-113 by wet air oxidation. Since supercritical water oxidation is touted as faster than wet air oxidation, it may be capable of more efficient destruction of CFCs and halons.

- CONS: Destruction of CFCs or halons by supercritical water oxidation is untested and unproven. The possibility of high energy consumption and possible metallurgical limitations are unresolved concerns.

## CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **WET AIR OXIDATION**

OPERATING PRINCIPLE: This process involves using a high temperature (temperature > 300°C (570°F)) aqueous stream with oxygen to destroy many organic compounds. With CFCs or halons, the destruction process might involve hydrolysis as well as oxidation.

DEVELOPMENT STATUS: Commercial (For CFCs: Bench-scale)

DESTRUCTION EFFICIENCY: High, but limited to aqueous streams only.

RELIABILITY/OPERABILITY: Possible metallurgy considerations which might affect reliability/operability and cost.

SECONDARY ENVIRONMENTAL CONCERNS: Unknown; possible neutralization of acidic aqueous waste stream. Fluoride salts are a potential concern.

COSTS - CAPITAL: Possible requirement for exotic materials of construction.

- OPERATING AND MAINTENANCE: High energy requirements due to high temperature. Requires oxygen supply.

LIMITATIONS/BARRIERS: Wet air oxidation is typically used with aqueous streams only. Since CFCs and halons do not have an abstractable hydrogen or a double bond, they are resistant to oxidation. This may make them difficult to destroy using this process.

SUMMARY - PROS: Limited data exist for destruction of CFC-113 by wet air oxidation. Effective on aqueous streams. May be able to enhance by adding solid catalyst.

- CONS: Possible limitation to dilute aqueous streams only. Wet air oxidation may be considered slow compared to other types of destruction processes.

## CONTROL TECHNOLOGY SUMMARY

TECHNOLOGY NAME: **CORONA DISCHARGE**

OPERATING PRINCIPLE: This process uses a high voltage AC or DC discharge to generate an ionized corona field. The energized electrons are capable of dissociating many types of hazardous wastes.

DEVELOPMENT STATUS: Bench-scale

DESTRUCTION EFFICIENCY: High, when several stages are connected in series to obtain long residence times.

RELIABILITY/OPERABILITY: Insufficient data to estimate reliability and operability.

SECONDARY ENVIRONMENTAL CONCERNS: Possible modification to the basic design may offer potential for simultaneous destruction and neutralization. Otherwise, the acid gases generated as a result of CFC/halon destruction would have to be scrubbed and neutralized.

COSTS - CAPITAL: Could require multiple stages. Power supply may be expensive.

- OPERATING AND MAINTENANCE: Possible high electrical costs.

LIMITATIONS/BARRIERS: The process is still in development phase. Current research efforts are directed towards modeling the corona field and scaling up the technology. Also, studies to establish power consumption as a function of destruction efficiency are needed, as well as investigating the properties of an ionized bed of reactive pellets.

SUMMARY - PROS: The corona destruction process is fairly rapid, and is performed at ambient temperatures and pressures. The possibility of simultaneous destruction and neutralization is potentially valuable, but unproven.

- CONS: Destruction of CFCs or halons in a corona discharge is untested. The possibility of high power consumption and difficulty in modeling and scaling up to commercial size are unresolved concerns.

## APPENDIX C

## List of Technologies

(Listing of all technologies considered for destruction of hazardous wastes to determine applicability towards CFC and halon destruction)

LEGEND FOR CODES:

1. Waste Streams

| | |
|---|---|
| G | Gas |
| L | Liquid |
| S | Solid |
| Sl | Sludge |

2. State of Development

| | |
|---|---|
| Co | Conceptual |
| B | Lab or Bench scale |
| P | Pilot scale |
| C | Commercial |
| C* | Commercial on other than hazardous wastes |

3. Applicable to CFCs

| | |
|---|---|
| 1 | Data available for CFCs |
| 2 | No data for CFCs but appears feasible |
| 3 | Doubtful application |

| General Category | Process Name | Description | Waste Stream | State of Development | Applicable to CFCs | Contact |
|---|---|---|---|---|---|---|
| THERMAL PROCESSES | Infrared Thermal Destruction | Wastes are metered on a woven belt and pass under an infrared heating element. Combustible off-gases are burned in a secondary chamber. | S | C | 3 | ECOVA, Inc. (formerly Shirco), Dallas, TX |
| | Circulating Fluidized Bed Combustor | Uses injection of limestone to neutralize acid gases. | L,S,Sl | C | 1 | Ogden Environmental Services, San Diego, CA |
| | Multisolid Fluidized Bed | Uses a moving bed of heated inert material to incinerate wastes. | All | C* | 3 | Battelle Memorial Institute, Columbus, OH |
| | Advanced Electric Reactor | Performs well only on finely ground material. Technology is currently shelved. | S | C | 2 | J.M. Huber, Co. Borger, TX |
| | Fluid Wall Reactor | Uses electrically induced radiant heat to pyrolyze organic constituents. Same as Huber technology. | S | Unk | 2 | Thagard Research Corp. Costa Mesa, CA |
| | Electric Pyrolyzer | Reaction chamber heated to 3000 F where organics are volatilized and solids are vitrified. | S | Unk | 3 | Westinghouse Madison, PA |
| | Pyroplasma System | Doing extensive testing with commercial scale equipment in the laboratory. Wastes must be pumpable. | L,Sl | P | 2 | Westinghouse Madison, PA |
| | Plasma Pyrolyzer | Built around the Westinghouse torch. Currently not working with this technology. | L,Sl | P | 2 | Pyrolysis Systems Niagara Falls, Ontario Canada |
| | Pyrolytic Decomposition | Heats waste materials in the absence of oxygen to drive off volatiles for incineration or recovery. | L,Sl | C | 3 | Midland-Ross Corp Toledo, OH |

| General Category | Process Name | Description | Waste Stream | State of Development | Applicable to CFCs | Contact |
|---|---|---|---|---|---|---|
| THERMAL PROCESSES (cont.) | High Temperature Pyrolysis with O2 | Uses oxygen induced high temperature to pyrolyze waste. | L,S | C* | 2 | Russell and Axon St. Louis, MO |
| | Applied Energetics Plasma Temperature Incinerator | Burns wastes in a pressurized stream of preheated oxygen. | L,S | P | 2 | Applied Energetics, Inc. Tullahoma, TN |
| | Joule Heated Glass Melter | Applies electric current directly to waste material for combustion and for creation of a glass matrix. | L,S | P | 3 | Battelle Pacific NW Labs Richland, WA |
| | Electromelt Pyro Converter | Uses a bed of molten glass to oxidize organics and to capture ash and inorganics. | L,S | C* | 3 | Penberthy Electomelt International, Inc. Seattle, WA |
| | Consertherm Rotary Kiln | A modular controlled air incinerator. | L,S,Sl | C | 2 | Industronics, Inc. South Windsor, CT |
| | Fast Rotary Reactor | A rapidly rotating cylinder using dryer technology for waste incineration. | S,Sl | P | 3 | PEDCo Technology Corp Cincinnati, OH |
| | "Cyclin" Cyclone Incinerator | A cylindrical shaped combustion chamber provides for intensive mixing of fuel and air. | G,L | C | 2 | Institute of Gas Technology, Chicago, IL |
| | Pyretron Oxygen-enhanced burner | Oxygen enhancement allows higher feed rates while still maintaining performance. | G,L | C | 2 | American Combustion |
| | Liquid Injection Incineration | Common technology. | L | C | 1 | Several |
| | Thermal and Catalytic Incineration | Common technology. | G | C | 1 | Several |

| General Category | Process Name | Description | Waste Stream | State of Development | Applicable to CFCs | Contact |
|---|---|---|---|---|---|---|
| CHEMICAL PROCESSES | Wet Air Oxidation | Uses elevated temperature and pressure to oxidize organics in water. | Aq | C | 1 | Zimpro Environmental Systems, Rothschild, WI |
| | IT Catalyzed Wet Air Oxidation | Uses selective catalysts and elevated temperature and pressure to oxidize organics. | Aq | B | 2 | IT Envirosciences, Inc Knoxville, TN |
| | High Temperature Wet Oxidation | Uses long vertical underground tubular reactor to oxidize suspended organics in water. | Aq | Co | 2 | Methods Engineering Inc. Angleton, TX |
| | Supercritical Fluid Oxidation | Uses high temperatures and very high pressures to oxidize organics. | L | P | 2 | MODAR, Inc. Natick, MA |
| | Molten Salt Destruction | Uses a bed of molten sodium carbonate to destroy wastes and scrub acid gases. | L,S | P | 2 | Rockwell International Canoga Park, CA |
| | Metal Oxide Destruction | Uses an inexpensive metal oxide (such as alumina, Al203) to react with CFCs at 500 to 800 deg C. | G | Co | 2 | Dr. Dan Blake SERI 1617 Cole Blvd. Golden, CO 80401 |
| | Battelle Northwest Aqueous Phase Alkaline Destruction of Halogenated Organics | Converts halogenated organics into an oil using mild alkali under pressure | L,S | B | 2 | Battelle Pacific Northwest Laboratories P.O. Box 999 Richland, WA 99352 |
| | GARD Catalytic Dehalogenation of Hazardous Wastes | Dehalogenizes compounds by replacing halogen atom with hydrogen atom. | L | B | 2 | Chamberlain National GARD Division 7501 N. Natchez Ave. Niles, IL 60648 |
| | Acurex Process | Sodium reagent with a proprietary constituent reacts to form NaCl and nontoxic product. | L,Sl | C | 2 | Acurex P.O. Box 13109 Research Triangle Park, NC 27709 |

| General Category | Process Name | Description | Waste Stream | State of Development | Applicable to CFCs | Contact |
|---|---|---|---|---|---|---|
| CHEMICAL PROCESSES (cont.) | PPM Process | Uses a proprietary sodium reagent to dechlorinate organic molecules. Can not be used on aqueous streams. | L | | 3 | |
| | Sunohio PCBX | Uses proprietary reagent to convert PCB molecules to metal chlorides and polyphenol compounds | | P | 3 | |
| | Potassium polyethylene glycolate (KPEG) wash | Effective in dehalogenating aromatics and aliphatic organic materials. Has been tested on wood preservatives and spent solvent with dioxin. | L | P | 2 | |
| | Ozonation | Injection of ozone to react with organics and form nontoxic materials | L,Sl | C | 3 | Several |
| | UV photolysis/APEG * detoxification *(alkaline polyethylene glycols) | UV radiation is used to convert halogenated materials. Needs a hydrogen donor. | | | 2 | IT Enviroscience Knoxville, TN |
| BIOLOGICAL PROCESSES | Biological Degradation | Microbes are injected into the ground or ground removed and slurried with organisms. Will be demonstrated with pentachlorophenol and creosote wastes. | S | | 3 | DETOX Industries, Inc. Sugarland, TX |
| | Fluid bed biological Systems | | | | 3 | Air Products & Chemicals Allentown, PA |
| | Liquid/solid contact digestion | | | | | Motec, Inc. Mt. Juliet, TN |

| General Category | Process Name | Description | Waste Stream | State of Development | Applicable to CFCs | Contact |
|---|---|---|---|---|---|---|
| BIOLOGICAL PROCESSES (cont.) | Ion exchange (biological) | | | | 3 | Sunitech, Inc. Twinburg, PA |
| | Powdered activated carbon (biological) | | L | C | 3 | Zimpro Environmental Control Systems Rothschild, WI |
| | White Rot Fungus (Phanerochaete chrysosporium) | Used to degrade lignin, but is also effective in degrading organo-halides. | | B | 3 | |
| | Pseudomonas cepacia (AC1100) | Developed to dechlorinate a variety of chlorophenols. | | B | 3 | |
| | Pseudomonas putidas | Developed for PCB degradation | S | Unk | 3 | General Electric |
| | Activated sludge | Common technology | All | C | 3 | Several |
| ELECTRICAL PROCESSES | Corona Discharge | High energy electrons are capable of dissociating the compounds of interest. | G | B | 2 | Dr. Norm Plaks U.S. EPA/AEERL Research Triangle Park, NC 27711 |
| OTHER PROCESSES | Solar Destruction | Solar energy is focussed to generated high temperatures. | L | P | 2 | Dr. Hugh Reilly Sandia National Lab Albuquerque, NM 87185 |
| | Microwave discharge | Similar to incineration | G | Unk | 3 | |

## APPENDIX D

### Trial Burn Data Table

(Data for destruction efficiency collected from trial burn testing for RCRA Part B permit)

RCRA PART B TRIAL BURN TEST DATA SUMMARY

| Facility Name (Type of Incinerator) | Location | Test Number | Type of Feed | Waste Feed Concentration (Percent) | Destruction Efficiency (Percent) | Temperature (Deg F) | Test Date | Source |
|---|---|---|---|---|---|---|---|---|
| Olin (Liquid Injection) | Brandenburg, KY | No. 2 | CFC-11 | 10.3 | >99.9998 | 2,088 | 11-28-84 | (A) |
| | | No. 2 | CFC-12 | 5.8 | >99.9998 | 2,088 | 11-28-84 | (A) |
| | | No. 3 | CFC-11 | 14.0 | >99.9999 | 2,095 | 11-29-84 | (A) |
| | | No. 3 | CFC-12 | 5.6 | >99.9998 | 2,095 | 11-29-84 | (A) |
| Pennwalt (Liquid Injection) | Calvert City, KY | No. 22-1 | HCFC-141b | 8.9 | 99.997 | 2,220 | 12-3-83 | (A) |
| | | No. 22-2 | HCFC-141b | 10.2 | 99.995 | 2,220 | 12-4-83 | (A) |
| | | No. 22-3 | HCFC-141b | 17.6 | >99.999 | 2,220 | 12-5-83 | (A) |
| | | No. 22-4 | HCFC-141b | 15.0 | >99.999 | 2,220 | 12-9-83 | (A) |
| | | No. 23-1 | HCFC-141b | 9.2 | >99.999 | 2,300 | 12-6-83 | (A) |
| | | No. 23-2 | HCFC-141b | 15.1 | >99.999 | 2,300 | 12-7-83 | (A) |
| | | No. 23-3 | HCFC-141b | 14.5 | >99.999 | 2,300 | 12-8-83 | (A) |
| GSX/Thermal Oxidation Corp. (Liquid Injection) | Columbia, SC | No. 3 | CFC-11 | 8.3 | 99.999 | 1,800 | 3-19-87 | (B) |
| Honeywell (Liquid Injection) | Pinellas Co., FL | No. 1 | CFC-112 | 0.71 | >99.9999 | 1,788 | 6-14-88 | (B) |
| | | No. 2 | CFC-112 | 0.71 | >99.9996 | 1,819 | 6-14-88 | (B) |
| | | No. 3 | CFC-112 | 0.71 | >99.9999 | 1,799 | 6-15-88 | (B) |
| LWD (Rotary Kiln) | Calvert City, KY | No. 1 | CFC-11 | 3.0 | 99.994 | 1,861 | 12-14-88 | (B) |
| | | No. 2 | CFC-11 | 3.6 | 99.9995 | 1,828 | 12-14-88 | (B) |
| | | No. 3 | CFC-11 | 3.9 | 99.9917 | 1,640 | 12-15-88 | (B) |
| LWD (Liquid Injection) | Calvert City, KY | No. 2 | CFC-11 | 2.8 | 99.9801 (1) | 1,647 | 12-16-88 | (B) |
| Rollins Environmental (Rotary Kiln) | Bridgeport, NJ | No. 1 | HCFC-22 | -- | 99.9993 | -- | 6-7-88 | (C) |
| | | No. 2 | HCFC-22 | -- | 99.9997 | -- | 6-8-88 | (C) |
| | | No. 3 | HCFC-22 | -- | 99.9985 | -- | 6-8-88 | (C) |
| Pennwalt (2,3) | Thorofare, NJ | -- | HCFC-141b | -- | -- | 2,000 | -- | (C) |
| ICI (3) | Bayonne, NJ | -- | HCFC-22 | 23.6 | -- | 2,300 | -- | (C) |
| | | | CFC-11 | 7.1 | | | | |
| | | | FC-1114 | 13.9 | | | | |
| DuPont (3) | Deepwater, NJ | -- | CFC-113 | 10.0 | -- | 2,000 | -- | (C) |

SOURCES

A. Permit Writers Guide to Test Burn Data
B. RCRA Part B Permit File Search at EPA Region 4 (Atlanta, GA)
C. Hazardous Waste Facility Permit File Search at New Jersey Department of Environmental Protection (Trenton, NJ).

NOTES

1. According to plant, low destruction efficiency was due to a portion of waste feed CFC-11 was contained in glass bottles which remained partially intact.
2. This is a duplicate of Pennwalt's unit in Calvert City, KY.
3. Test results have not yet been reported.

## APPENDIX E

### List of Contacts

(List of Contacts by letter or phone with date, name, organization, and brief summary)

| DATE | NAME | ORGANIZATION | SUBJECT |
|---|---|---|---|
| 2/27/89 | Dr. Barry Dellinger | University of Dayton Research Institute | Discussed difficulties in destroying CFCs and formation of PICs. |
| 2/27/89 | Mr. Ed Lukosius | E.I. DuPont de Nemours | Requested any information that DuPont may have developed on destruction technologies. |
| 2/27/89 | Mr. Gene Irrgang | T-Thermal | Requested information on experience T-Thermal has in CFC incinerator field. Mr. Irrgang did not want disclose info without assurances of secrecy. He felt that PICs are not a problem for well-run unit. |
| 2/28/89 | Mr. Frank Dwyer | Allied/Signal | Requested any information on destruction of CFCs or halons. Mr. Dwyer said that Allied has not been very active in the area. Another division of the company (Baron Blakeslee) has been more active in recovery of CFCs. |
| 3/3/89 | Mr. Wayne Fisher | Chemical Waste Management | Planning a trial burn in April 1989 which will include CFCs in the waste feed. |
| 3/3/89 | Mr. Gary Trivedi | LWD Incorporated | Recently performed a trial burn with CFC-11. Preliminary results indicate a DRE of 99.99%. |
| 3/6/89 | Mr. Joe Santoleri | Four Nines, Inc. | Assisted Pennwalt on their trial burn with HCFC-142b. Suggested EPA publication "Permit Writers Guide to Trial Burn Data." |
| 3/6/89 | Mr. Marshall Turner | Racon | Racon does not incinerate any off-spec product or still bottoms. Instead, they recycle back to the reactor. Trade-off versus incineration since they require more frequent catalyst changeout. |

| DATE | NAME | ORGANIZATION | SUBJECT |
|---|---|---|---|
| 3/6/89 | Dr. Mike Harris | ICI Americas | ICI does not incinerate any CFCs or halons at their U.S. halon plant. Later, he said that ICI does pyrolyze CFC-22 in a polymer production facility in Bayonne, NJ. |
| 3/6/89 | Mr. Mark Sweval | Great Lakes Chemicals | Great Lakes Chemical recycles about 95% of their off-spec or waste materials. They are looking into destruction processes with a professor at Purdue. |
| 3/6/89 | Mr. Rick Turner | LaRoche Chemicals | LaRoche does not incinerate any CFCs or halons. Mr. Turner raised the issue that contaminated CFCs may be classed as hazardous wastes. |
| 3/7/89 | Mr. Scott Kuhn | GSX Thermal Oxidation Corp. | Mr. Kuhn said that CFC-11 was included in a trial burn at their facility in Columbia (SC). He suggested contacting Ms. Betty Willis with EPA Region 4 (Atlanta, GA). |
| 3/7/89 | Ms. Betty Willis | EPA Region 4 | Ms. Willis was aware of the GSX trial burn and said that results were on file in Region 4. She also suggested contacting Kathy Fore (Martin Marietta-DOE at Oak Ridge (TN)) or Teri Schearer (EPA/ORD at Cinncinati (OH)). They are developing a database with trial burn data. |
| 3/7/89 | Mr. Robert Vlick | Air Conditioning Co. | Mr. Vlick explained how his firm (a large chiller service organization) uses recycling with Omega to reduce the cost of refrigerant. |
| 3/7/89 | Mr. Mike Keller | John Zink Co. | Mr. Keller disputed T-Thermal's claim to being the only company in the world with experience with high concentrations of CFCs in incinerator waste feeds. |

| DATE | NAME | ORGANIZATION | SUBJECT |
|---|---|---|---|
| 3/7/89 | Mr. Jack Buice | Dow Chemical USA | Mr. Buice has extensive experience in thermal oxidation of chlorocarbons. He said that Dow has burned some fluorinated compounds in the past; he thought it was a CFC-contaminated oil. |
| 3/7/89 | Mr. Leo Weitzmann | Acurex | Mr. Weitzmann was knowledgeable about several types of chemical destruction processes for halogenated organics. He felt that active metals reaction has good potential for destruction of CFCs and halons. |
| 3/7/89 | Mr. Bill Scofield | Chemical Waste Management | Mr. Scofield explained how their Port Arthur (TX) facility handles wastes containing CFCs. They are limited to 100 ppm fluoride in the waste feed, so they can blend on-site to dilute wastes with a high CFC concentration. |
| 3/8/89 | Mr. John Backlund | Coen Company | Mr. Backlund explained that Coen Co. designed the burners for a shipboard incinerator which was able to handle all types of waste feeds. He said that one advantage of shipboard incineration was that a stack scrubber system wasn't needed. |
| 3/9/89 | Mr. Dennis O'Meara | Omega Recovery | Mr. O'Meara felt that there was essentially no reason to destroy contaminated CFCs. He claimed nearly everything could be recycled economically. |
| 3/13/89 | Mr. Jim Aker | E.I. DuPont de Nemours Chambers Works | Mr. Aker said that DuPont has just completed a trial burn on a new incinerator at the Chambers Works which handles up to 10% CFC & other fluorine-containing wastes. Data is not yet available. |
| 3/14/89 | Dr. James Spivey | Research Triangle Institute | Dr. Spivey has worked on catalytic incineration of chlorinated organics. He suggested two commercial vendors (ARI & Dedert Topsoe). |

| DATE | NAME | ORGANIZATION | SUBJECT |
|---|---|---|---|
| 3/14/89 | Mr. Leon Leonard | Radian Corporation (Sacramento) | Mr. Leonard checked on the status of Omega Recovery project in Kern Co. (CA), which was to include some type of incinerator for solvent wastes. He said the project had been effectively halted because of permitting problems. |
| 3/14/89 | Mr. Per Bakken | Norway Ministry of Environment | Mr. Bakken said that he was unaware of anything in Norway in the area of CFC or halon destruction. |
| 3/17/89 | Mr. Tom Hedlund | Swedish National Enviromental Protection Board | Mr. Hedlund explained that they are looking at two issues in terms of destruction. First, they are investigating the destruction of refrigerators and freezing equipment. Second, they are part of an inter-Nordic project to investigate destruction of CFCs and halons. So far, results are only for lab-scale tests. |
| 3/17/89 | Mr. Wolfgang von Klahr | Hoechst/Celanese | Mr. von Klahr explained that their parent company in Germany (Hoechst AG) has a unit for complete combustion of CFCs. Follow-up info from Sigri Elektrographit (a subsidiary of Hoechst) provided a European patent number and limited data. |
| 3/20/89 | Dr. Vic Cundy | Louisiana State University | Dr. Cundy has been working on incineration of chlorinated methanes, but hasn't looked at CFCs or halons. Despite the similarities, the models which have been developed for chloroform or methylene chloride cannot be simply extended to CFCs. |
| 3/22/89 | Mr. Bob Foster | Pennwalt (Calvert City, KY) | Mr. Foster explained that their facility handles only materials from HCFC-142b production. Neither CFC-11 or CFC-12 wastes are burned, and they do not produce CFC-113. He said the unit in Thorofare, NJ is a duplicate of the Calvert City unit. |

| DATE | NAME | ORGANIZATION | SUBJECT |
|---|---|---|---|
| 3/23/89 | Mr. James Hemby | U.S. EPA (Washington, DC) | Mr. Hemby said he could provide updated estimates of the U.S. and world bank of CFCs and halons. |
| 3/23/89 | Ms. Laura Tew | Olin Corporation | Ms. Tew explained that Olin incinerates waste from a urethane blending facility operated by Olin. They are also permitted to accept commercial waste, they do so only on a limited basis. They monitor CO on a continuous basis. |
| 3/24/89 | Mr. S. Misaki | Daikin Industries, Ltd. | Mr. Misaki explained that in general, processes which could or are being used for CFC destruction include conversion to monomer for fluoroplastics, incineration, or possible reaction with metal oxide. |
| 3/27/89 | Dr. Dean Walbach | Acurex | Dr. Walbach said that he has tested solvent cleaning equipment for CFC emissions, but no incinerators. He didn't see any special problems, and he thought the VOST method would work best. |
| 3/28/89 | Mr. John Scott | New Jersey Department of Environmental Protection - Hazardous Waste Engineering Dept. | Mr. Scott said that Rollins Environmental trial burn report lists CFC-113 among the PICs, but was not included in the feed POHCs. He suggested checking the document "Guidance on Trial Burn Reporting and Setting Permit Conditions" by Acurex Corp. |
| 3/30/89 | Mr. Swager | Netherlands (Environmental Board) | Mr. Swager provided information on Netherland's joint venture for hazardous waste incineration in Rotterdam. The facility opened in 1987 and is equipped with the most modern rotary kiln and stack gas cleaning equipment. They are planning to double capacity by expanding the scrubbers in 1991. Waste feed limits are 5.8% Cl & 0.58% F. |

# APPENDIX F

## Japanese MITI Attachment

(Overview of current research efforts in Japan to evaluate CFC and halon destruction technologies.)

March 2, 1989

# Technologies for the Destruction of Chlorofluorocarbons*

by

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Agency of Industrial Science and Engineering
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The destruction of chlorofluorocarbons (CFCs) has been regarded as difficult technology. One of the reasons is that CFCs are inflammable and chemically stable. Secondly the released halogen from CFCs, in particular, fluorine species as HF, $F_2$, or any other intermediates, is difficult to treat with. Little reports have been published and most results are fundamental because the destruction has not been required until the global environmental problems of stratospheric ozone depletion and climate changes were pointed out.

The feasible technologies for the destruction are classified into following four categories. Active works to develop the destruction of CFCs are currently promoted in Japan.

## 1. Incineration and Thermal Decomposition

Incineration of CFC-113 was reported to be performed at 800°C with 99.99% efficiency. However, analysis of trace products were not reported. In Japan thermal decomposition of CFCs adsorbed on an activated carbons was carried out under nitrogen stream. The conversion of CFCs were almost 100% below 800°C. However, CFC-11 and CFC-12 were converted to considerable amount of $CF_4$, which was not further decomposed below 800°C. The incineration and thermal decomposition are low-cost destruction methods, but released halogen attacks the furnace surface. The materials of furnace are to be improved. It is also important to analyze trace of hazardous by-products.

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## 2. Catalytic Decomposition

Reportedly an activated carbon catalyzed the decomposition of CFC-11 under dilute concentrations. In Japan research has revealed that some solid catalysts also accelerated the decomposition of CFC-113 at above 300°C. Over these catalysts conversion more than 60% was attained in a stream of 1000 ppm. On raising the reaction temperature or increasing catalyst amount, 100% conversion will be easily obtained. $CO_2$, HCl and HF were detected. The analysis of trace by-products is under investigation.

Photo-catalytic decomposition of CFC-11 took place on some transition-metal oxides such as titanium dioxide at around room temperature, although the conversion rate was slow. Platinum loaded on titanium dioxide accelerated the decomposition.

Catalysis is one of the promising methods for the selective decomposition of CFCs at relatively low temperatures. The converter is designed to be compact apparatus as compared to the incineration.

## 3. Plasma Decomposition

Plasma reactor provides reactive species from stable compounds. Recently in Japan the effectiveness for the decomposition of CFCs was confirmed on thermal plasma at ca. 10000°C. The CFCs are decomposed efficiently and surely, as demonstrated that conversion more than 99.7% achieved, although apparatus is not low-costed. HCl, HF, $CO_x$, and carbonaceous materials were formed from CFCs and water mixture.

Low-temperature (non-equilibrium) plasma may give only partial decomposition, since it was reported to give mainly acetylene, carbon monoxide and solid carbon from trichloroethylene and water mixture.

## 4. Chemical Reaction Using Reagents

In Japan a reducing agent of sodium naphthalene complex ($Na^+Naph^-$) and CFCs was found to afford stoichiometric reaction. In batch experiments reaction between $Na^+Naph^-$ and CFC-113 at 150°C

indicated 100% conversion of CFC-113. Continuous reaction is under investigation. The destruction method is improved by (1) finding low-cost reducing agents and (2)increasing selectivity to CFCs in a mixture of CFCs and other reactive materials. It is necessary to confirm that no hazardous products are formed in the reaction.

## 5. Other Methods

There are many other methods for the detoxicification of halocarbons, which include electrochemical reaction, UV-irradiation, and X-ray irradiation. These were only applied to chlorocarbons. To our knowledge no report is found on the destruction of CFCs.

## 6. Conclusions

Many projects on the destruction of CFCs have started recently in Japan. From our experiences, the appropriate method for the destruction requires to satisfy following several items.

(1) The destruction is to be performed surely under the operational conditions of a wide range.
(2) No trace amounts of hazardous by-products are to be formed.
(3) Mixtures containing CFCs are to be decomposed selectively.
(4) Several kinds of destruction technologies are to be established depending on emission types of CFCs (gas, liquid, or solid; concentrated or dilute, etc.).

The above methods are easily applicable to the substitute materials of CFCs as well as chlorocarbons such as trichloroethylene, since they are more reactive than CFCs.

Table Consumption of CFCs in Japan (1987 estimated: in ton).

| | Refrigerants | Propellants | Blowing Agents | Solvents | Others | Total |
|---|---|---|---|---|---|---|
| CFC-11 | 2,597 | 4,677 | 23,110 | 301 | 230 | 30,915 (20.8%) |
| CFC-12 | 22,139 | 7,423 | 9,886 | 0 | 5 | 39,453 (26.6%) |
| CFC-113 | 270 | 180 | 200 | 73,136 | 1,910 | 75,696 (51.0%) |
| CFC-114 | 179 | 250 | 1,655 | 0 | 0 | 2,084 ( 1.4%) |
| CFC-115 | 170 | 0 | 0 | 0 | 0 | 170 ( 0.1%) |
| Total | 25,355 (17.1%) | 12,530 ( 8.4%) | 34,851 (23.5%) | 73,437 (49.5%) | 2,145 ( 1.4%) | 148,318 (100 %) |

# RESEARCH PROJECTS RELATED TO CFCs IN OUR INSTITUTE

National Research Institute for
Pollution and Resources
AIST, MITI

## ABATEMENT

1) Emission Control of Volatile Organic Halides by Adsorption.
   - Development of Adsorbents
   - Development of Recovery Method from Adsorbed Phase
   - Proposal of Adsorption System

2) Chemical Decomposition of CFCs.
   - Treatment of CFCs Waste
   - Treatment of Mixtures and Dilute Gas

3) Combustion of Hazardous Organic Waste Mixtures
   - Combustion Technology for Hazardous Wastes
   - Analyses of Trace Products from Combustion

## ASSESSMENT

1) Heterogeous Reactions of CFCs in the Atmosphere
   - Catalytic Reaction under Irradiation
   - Products Analysis of the Reaction

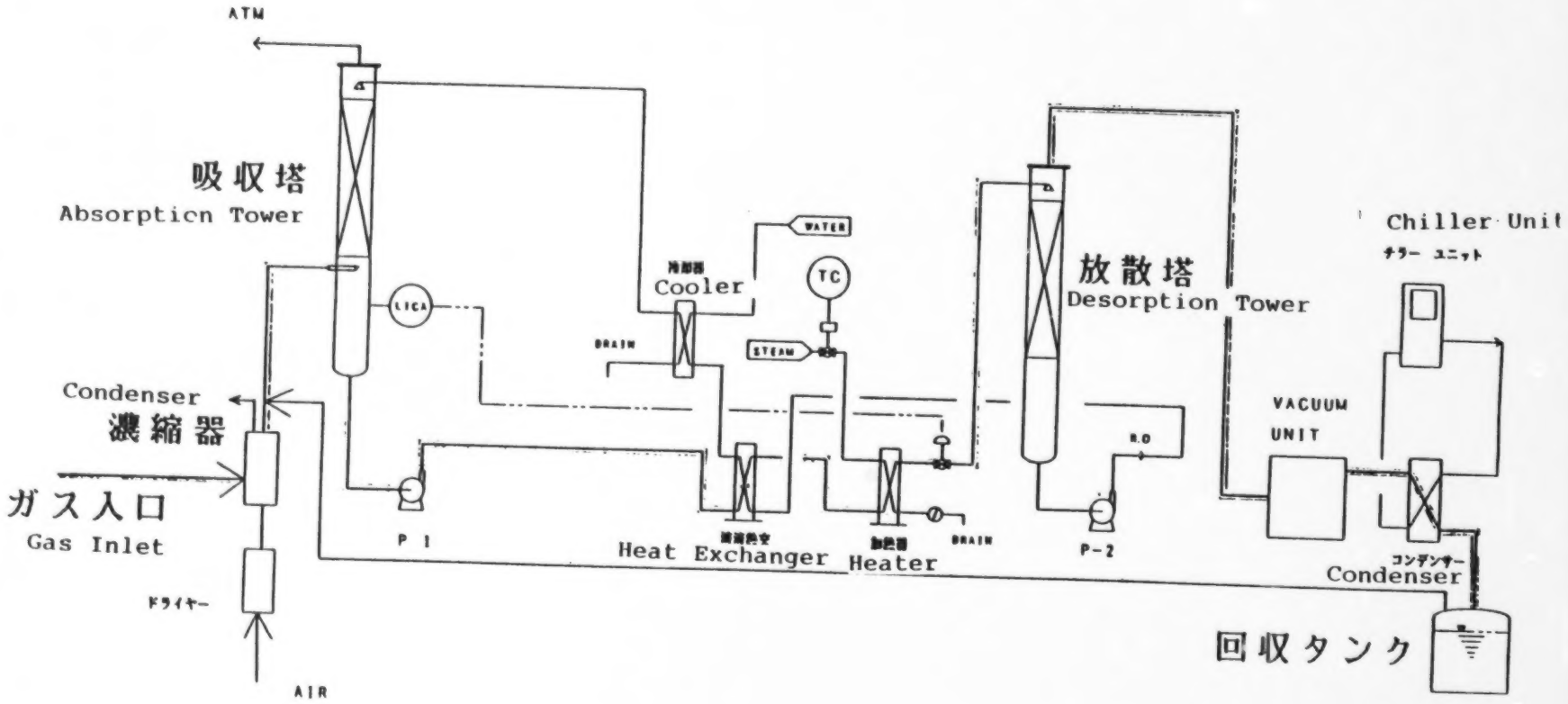
2) Reaction Process of Substitute CFCs in the Troposphere
   - Catalytic Reaction under Irradiation
   - Products Analysis of the Reaction

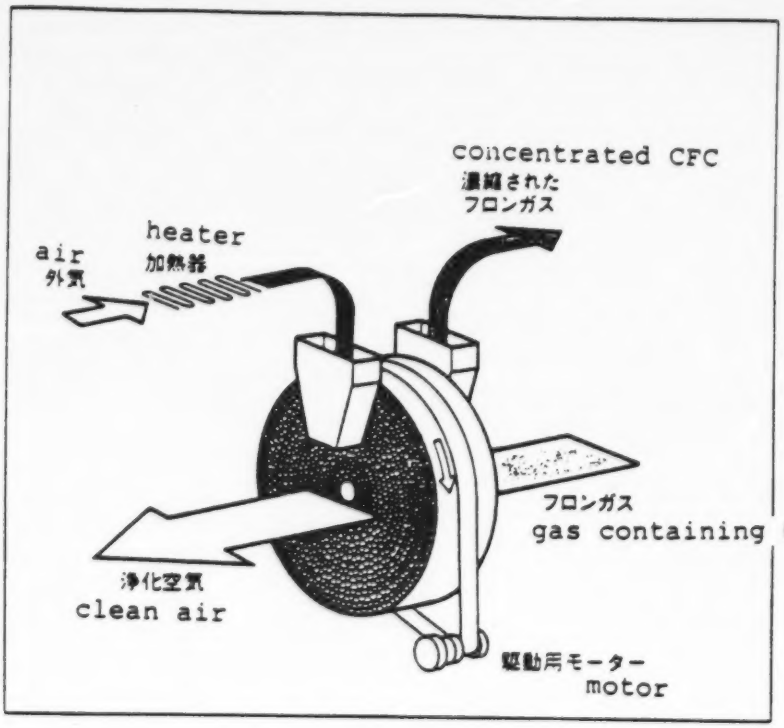
3) Behavior of Green-House Gases from Industry

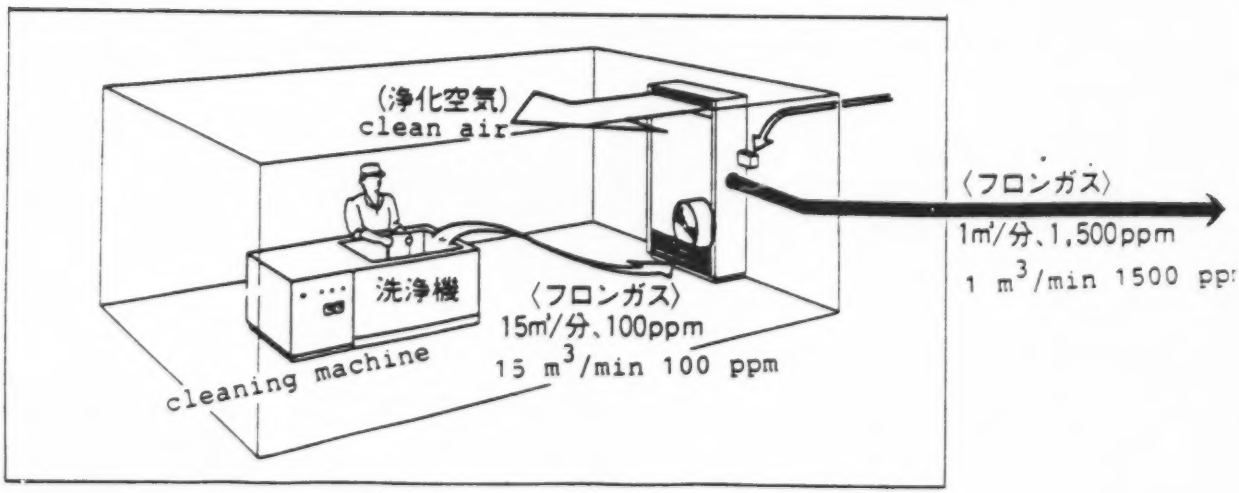
4) Diffusion and Monitoring of Pollutants Including CFCs from High-Tech Industry
   - Duffusion mechanism and modelling of pollutants in the atmosphere, ground suface and undergroud

# 吸収法の例

An EXAMPLE OF ABSORPTION

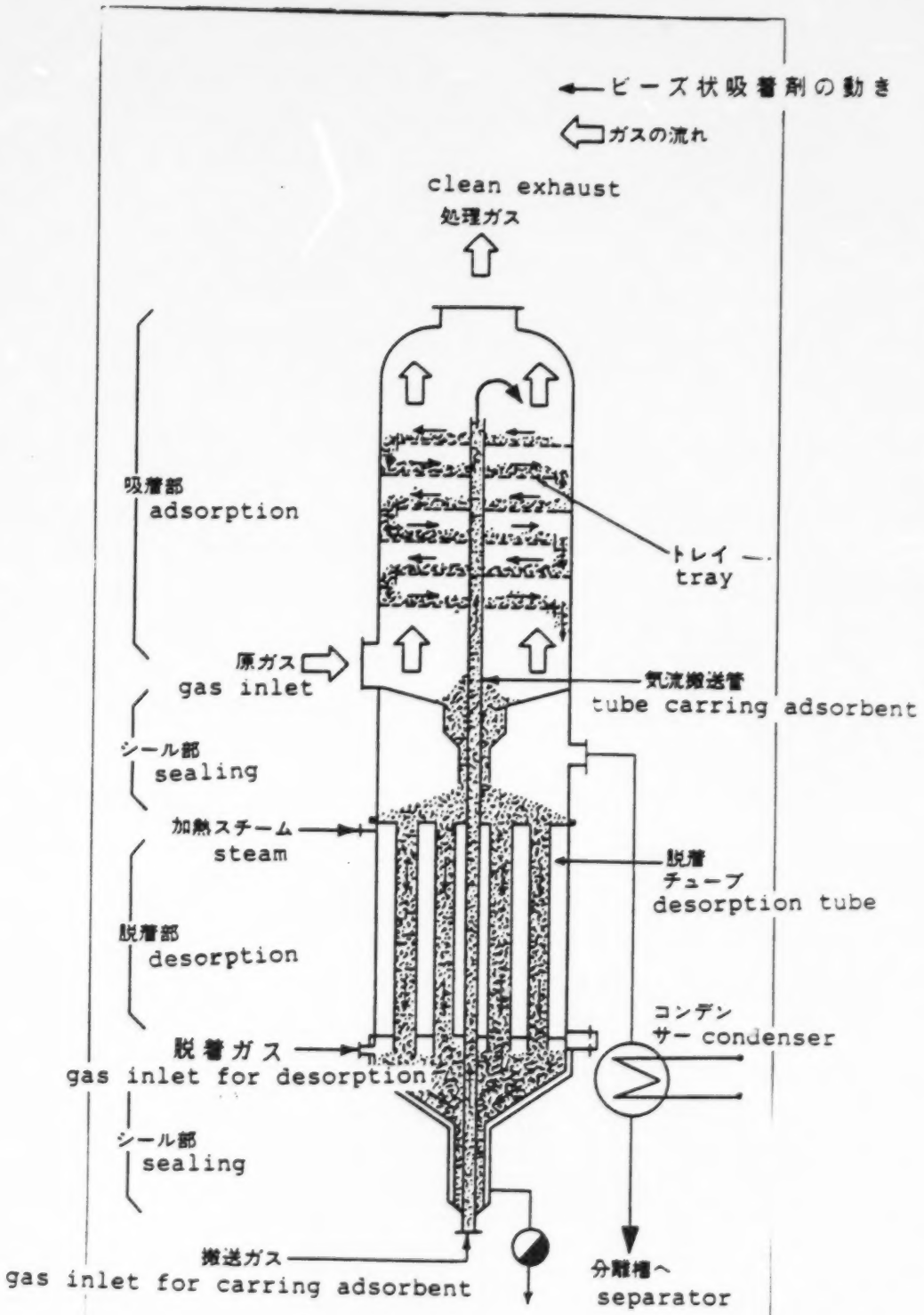




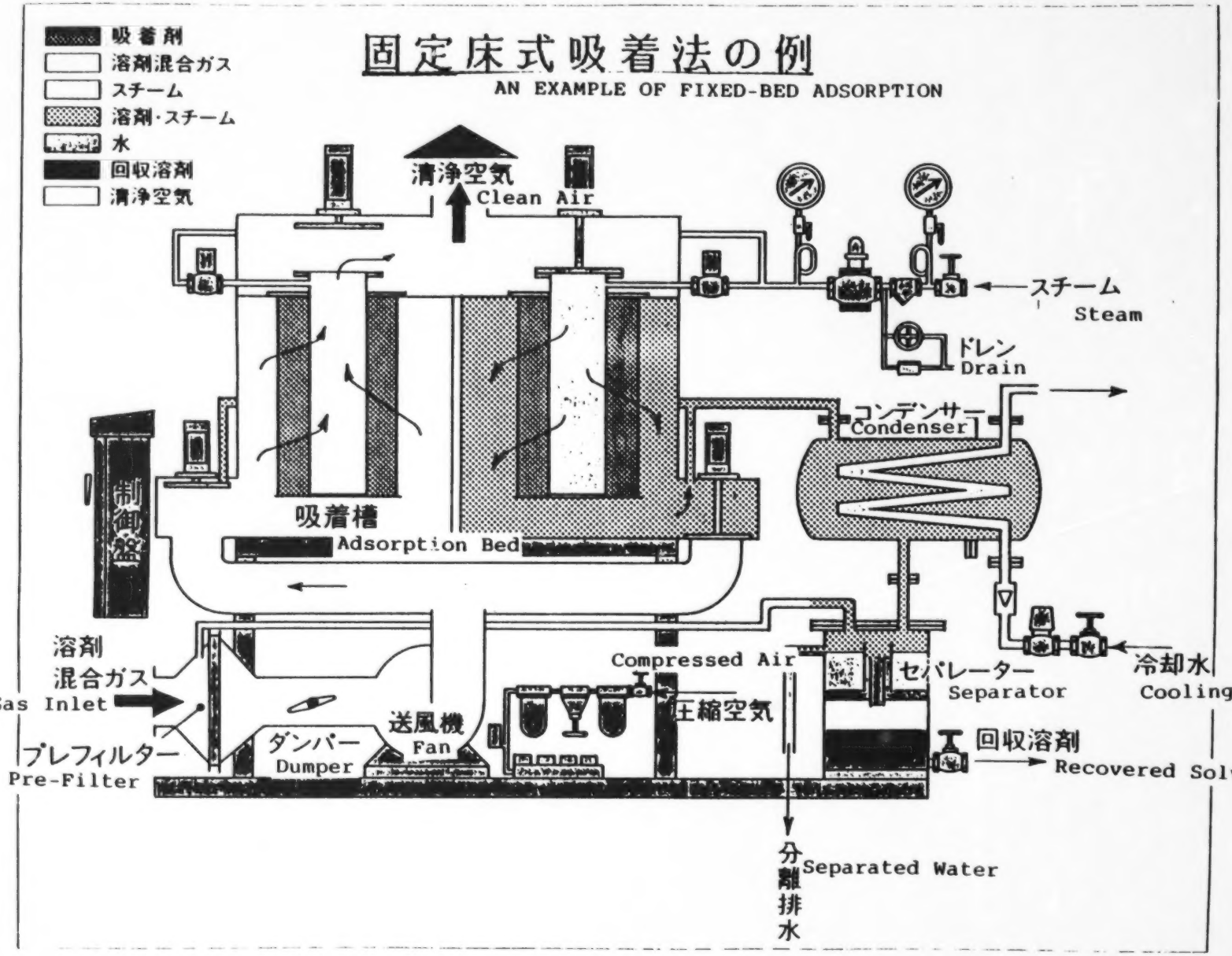

# 連続回転式吸着法の例

AN EXAMPLE OF ROTARY ADSORPTION




# 流動床式吸着法の例

AN EXAMPLE OF FLUIDIZED-BED ADSORPTION


吸着剤
溶剤混合ガス
スチーム
溶剤・スチーム
水
回収溶剤
清浄空気
固定床式吸着法の例
AN EXAMPLE OF FIXED-BED ADSORPTION
清浄空気
Clean Air
スチーム
Steam
ドレン
Drain
コンデンサー
Condenser
制御盤
吸着槽
Adsorption Bed
溶剤
混合ガス
Gas Inlet
プレフィルター
Pre-Filter
ダンパー
Dumper
送風機
Fan
Compressed Air
圧縮空気
セパレーター
Separator
冷却水
回収溶剤
Recovered Solvent
分離排水
Separated Water